

# MODIFIED KENAF VIA NICKEL NITRATE FOR HYDROGEN GAS STORAGE

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To my husband & daughter, families and fellow friends.

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## ABSTRACT

Hydrogen is one of the renewable energy sources that are viable as an alternative fuel source. Hydrogen fuel offers protection towards the environment. Hence, hydrogen storage is a necessity in order for hydrogen fuels can be used for mobile purposes. However, one of the major barrier for hydrogen fuels is the storage technique. To prevent high pressure problem during storing, kenaf as adsorptive hydrogen storage was introduced in this study. Since kenaf is a natural adsorbent with porous structure, modification with nickel metal for hydrogen adsorption process was conducted. The objectives of the study were to characterize kenaf and modified kenaf as adsorbents, to assess adsorptive capacity of the adsorbents and to assess delivery performance of the adsorptive gas storage. In this study, nickel nitrate ( $\text{Ni}(\text{NO}_3)_2$ ) was used to modify kenaf using nickel metal deposition method. The concentration of  $\text{Ni}(\text{NO}_3)_2$  was varied for each sample to determine the suitable amount of modifier for the kenaf sample. The pressure applied during the experiment was also varied in order to observe the delivery performance of the hydrogen adsorption. The physisorption occurred between hydrogen molecules and kenaf samples showed that modified kenaf was capable to adsorb more hydrogen as the hydrogen molecules was trapped within metal surface and kenaf surface itself. From this study, kenaf with 0.4 M of nickel (Ken-0.4MNi) showed better result in adsorbing hydrogen compared to raw kenaf sample. The specific area measurement for this sample was  $1.315 \text{ m}^2/\text{g}$  as it was a combination of mesoporous and macroporous structures. The field scanning electron microscopy micrograph of Ken-0.4MNi showed convincing surface structure for hydrogen molecules that had been adsorbed and stored since 0.4 M N-metal added improved the molecules arrangement in adsorbent. Based on the findings, Ken-0.4MNi could adsorbed  $15.0 \text{ mmol/g}$  hydrogen at pressure of 4 bar.

## ABSTRAK

Hidrogen adalah salah satu sumber tenaga boleh diperbaharui yang berdaya maju sebagai sumber bahan api alternatif dan dapat melindungi alam sekitar. Oleh itu, storan hidrogen adalah penting supaya bahan api hidrogen dapat digunakan dalam keadaan mudah alih. Walau bagaimanapun, salah satu halangan utama untuk bahan api hidrogen adalah teknik penyimpanannya. Bagi mengelakkan masalah tekanan tinggi semasa penyimpanan, kenaf sebagai storan gas hidrogen penyerapan telah diperkenalkan dalam kajian ini. Memandangkan kenaf adalah penyerap semula jadi dengan struktur berliang, pengubahsuaian dengan menggunakan logam nikel untuk proses penyerapan hidrogen telah dijalankan. Objektif kajian adalah untuk mencirikan kenaf dan kenaf yang diubahsuai sebagai penyerap, untuk menilai keupayaan penyerapan bahan penyerap dan menilai prestasi penghantaran storan gas penyerapan. Dalam kajian ini, nikel nitrat,  $(\text{Ni}(\text{NO}_3)_2)$  digunakan untuk mengubah suai kenaf menggunakan kaedah pengendapan logam nikel. Kepekatan  $\text{Ni}(\text{NO}_3)_2$  telah dipelbagaikan untuk setiap sampel bagi menentukan jumlah pengubah suai yang sesuai untuk sampel kenaf. Tekanan yang digunakan juga dipelbagaikan untuk memerhatikan prestasi penghantaran untuk penyerapan hidrogen. Penyerapan fizik yang berlaku di antara molekul hidrogen dan sampel kenaf menunjukkan bahawa kenaf yang diubah suai mampu untuk menyerap lebih hidrogen memandangkan molekul hidrogen telah terperangkap di dalam permukaan logam dan permukaan kenaf itu sendiri. Daripada kajian ini, kenaf bersama 0.4 M nikel (Ken-0.4MNi) telah menunjukkan hasil yang lebih baik dalam menyerap hidrogen berbanding sampel kenaf sahaja. Pengukuran luas tentu bagi sampel ini adalah  $1.315 \text{ m}^2/\text{g}$  merupakan kombinasi struktur liang meso dan liang makro. Mikrograf mikroskopi elektron pengimbas medan Ken-0.4MNi menunjukkan struktur permukaan molekul hidrogen terjerap dan tersimpan yang meyakinkan kerana penambahan 0.4MNi-logam memperbaiki penyusunan molekul dalam penyerap. Berdasarkan daripada hasil kajian, Ken-0.4MNi boleh menyerap  $15.0 \text{ mmol/g}$  hidrogen pada tekanan 4 bar.

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## LIST OF ABBREVIATIONS

H <sub>2</sub>	-	Hydrogen
LH <sub>2</sub>	-	Liquefied hydrogen
Ni-metal	-	Nickel metal
Ni(NO <sub>3</sub> ) <sub>2</sub>	-	Nickel nitrate
NKTB -	-	National Kenaf and Tobacco Board
NaOH	-	Sodium Hydroxide
HCHO	-	Formaldehyde
C <sub>2</sub> H <sub>6</sub> O	-	Ethanol
TGA	-	Thermogravimetric Analysis
FESEM	-	Field Analysis electron Microscopy
BET	-	Brunauer-Emmett-Teller
N <sub>2</sub>	-	Nitrogen
EDX	-	Electron Dispersive X-ray
CNG	-	Compressed Natural Gas
CO	-	Carbon Monoxide
CO <sub>2</sub>	-	Carbon Dioxide
FCV	-	Fuel Cell Vehicle
FCEV	-	Fuel Cell Electric Vehicle
LaNi <sub>5</sub>	-	Lanthanum-nickel alloy
TiCrMn	-	Titanium crystal
FeTi	-	Iron titanium hydride

**LIST OF SYMBOLS**

°C	-	degree Celcius
K	-	Kelvin
V	-	volume

## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Recent years, hydrogen fuel has been seen has a great potential as an energy source. Hydrogen can be generated from various sources, thus makes hydrogen the most available energy source in the universe. Hydrogen can be produced not only from fossil fuels, but also from wind, solar, thermal biomass with no pollution and form water as byproduct (Alves *et al.*, 2013). With various new technologies development, hydrogen is categorized as renewable energy fuel. At present, hydrogen is mainly used for vehicle. Hydrogen fuel for vehicle is mainly divided into three categories: Nickel-hydride battery, which is combined as a metal hydride; in a spark-ignition engine powered car; and in a fuel cell (Cheng *et al.*, 2012). However, hydrogen main problem is getting efficient storage technology.

Hydrogen has high energy capacity, with energy per unit of mass of 0.121 kJ/g, which is higher than any other substances. Nevertheless the demand for hydrogen kept increases since 2008. This is due to hydrogen great performance as energy fuel. For example, in oil sector, 364 billions/m<sup>3</sup> of hydrogen has been consumed and 409 billions/m<sup>3</sup> hydrogen consumption globally (Alves *et al.*, 2013). By 2013 onwards, it was estimated that the global hydrogen demand will increase to 18 % (Alves *et al.*, 2013). Hence, hydrogen energy demanding in various industries makes hydrogen as prime candidates to be used as power source in high technology development other than fossil fuels. However, its characteristic of lower density with 89.88 g/m<sup>3</sup> at stp makes storage of hydrogen fuel challenging.

Commercially, hydrogen storage has established three methods. There are high pressure gas storage, cryogenic hydrogen storage and adsorptive hydrogen storage. Due to low density of hydrogen, it requires a very high pressure (up to 700 bar) to store hydrogen gas (Zheng *et al.*, 2012; Teichmann *et al.*, 2012). For cryogenic hydrogen storage method, the tank or vessel could be filled up to 95 % of the tank. However, some space needs to be left due to prevent any embrittlement towards tank. These two types of methods are costly since it requires high technology with high pressure requirement for storage purposes. On the other hand, adsorptive hydrogen storage received attractive attention from researchers since it give better result in storing hydrogen with more economical cost. Devarakonda *et al.* (2012) have done a research for modeling and simulation on chemical hydride that has been used in adsorptive hydrogen storage. In their findings, by using ammonia borane (AB) as adsorbent, up to 16 % by weight could release 2500 mol/m<sup>3</sup> equivalent of hydrogen gas. Himmelberg (2010) has shown in his study that hydrogen could be released in high rate and extended from AB adsorbent in presence if either ionic liquid or bases. This shows that adsorptive material as potential efficient method for hydrogen storage. Moreover, adsorptive materials mostly are known for fuel cell application in transportation sector. The presence of chemical hydride could improve the ability of hydrogen adsorption with low pressure compared to high pressure gas storage method.

Metal hydride as adsorbent has attracted the developer in hydrogen adsorption field. In industry, this adsorbent has been widely used in order to store hydrogen gas. Pasini *et al.* (2013) has stated that Department of Energy US had simplified the on-board vehicle in order to use metal hydride as adsorptive hydrogen storage. Metal hydride such lanthanum-nickel alloy (LaNi<sub>5</sub>), Titanium crystal (TiCrMn) and iron titanium hydride (FeTi) has been attraction for over past 30 years to store hydrogen gas (Pasini *et al.*, 2013). These three types of metal hydride commonly used to reversibly store and deliver hydrogen for several transportation industries, but have been considered too heavy for nowadays commercial vehicle.

Hydrogen fuel storage has influenced the vehicle in various aspects including cost, performance and fuel economy. By using adsorbent materials, hydrogen

storage could be improved when more hydrogen molecules could attached onto adsorbent surfaces. By using adsorbent such as kenaf or *Hibiscus Cannabinus L.*, hydrogen storage may improve due to its light weight and high surface areas. Kenaf shows potential as fiber crop in various applications such as glass fiber composites. This bio-based has benefits farmers and could reduce non-renewable resources consumption. It is also safe for filling and delivering (Jimenez *et al.*, 2012) since kenaf is natural fiber. The particle size of kenaf (300  $\mu\text{m}$  to 500  $\mu\text{m}$ ) has shown its ability to adsorb gas since kenaf is widely used as oil absorbent in industry. For examples, in chemical industry, kenaf has been used to remove undesired chemical. This shows that kenaf contain good porous structure in its fiber since it being able to adsorb chemical or gas molecules.

Porous material such as kenaf has been introduced as new green technology in engineering. In general, the inner part of kenaf stalk which is kenaf core fiber has special characteristics as agro-based adsorbent since it has an internal porous structure to provide large surface area. Kenaf has potentially superior and cheaper adsorbent natural fiber and it known as biodegradable products, economically viable and ecologically friendly. With porous structure, kenaf has potential to be used as adsorptive material in gas storage. Zaveri (2004) in his research has identified that kenaf core particle gave high water absorbency depends on its particle size. This shows that kenaf core fiber could become alternative method for adsorption development. In order to improve kenaf characteristics as adsorptive hydrogen storage material, a functional group would be introduced to the surface of kenaf. Reports have proved that surface of adsorbents play important role in ehancing sorption capacity (D'Elia *et al.*, 2009; Paggiaro *et al.*, 2010; Yi *et al.*, 2011; Jimenez *et al.*, 2012).

## 1.2 Problem Statement

Adsorptive storage is one of the methods for storing hydrogen. By using adsorption process, physical adsorption of hydrogen forms a weak bond within pores. Adsorptive processes usually require highly porous materials in order to obtain



maximum surface area available for hydrogen sorption. It also requires easy uptake and release of hydrogen from the materials. By using suitable adsorbent, hydrogen gas could be adsorbed and store efficiently. The characteristic of adsorbent has influenced the performance of adsorption process. It includes the 500  $\mu\text{m}$  of particle size of adsorbent and its behavior on how it reacts with hydrogen molecules. There are few economical adsorbents are not suitable for hydrogen adsorption because of hydrogen characteristics, which are flammable. Excessive moisture that contain in adsorbent may be initiator for explosion occurred. Moreover, requirement on pressure of 700 bar for storing hydrogen gas in industry has demand more energy and costly. Therefore, new adsorbent in adsorptive method need to be introduced in order to make it reliable and more economical to the industry.

The use of kenaf as adsorptive material may reduce the storage pressure of the gas. In research and development, the capacity of hydrogen gas could be stored has become one of crucial part in storing gas. This is due to save more energy and space for secure use. Therefore, kenaf adsorbent has expected to become a new adsorbent that adsorb high amount of hydrogen. Since particle size of adsorbent has become one of the factors required, the adsorptive properties of kenaf need to be improved in order to maximize its storage capabilities. In this study, the particle size used for kenaf adsorbent was 500  $\mu\text{m}$  in size. For novelty, kenaf were modified using nickel in metal deposition method in order to improve its adsorptive ability. By using kenaf adsorbent, space for hydrogen storage could be reduced and capacity of hydrogen stored has expected to be better.

### **1.3 Objectives of Study**

Based on the above mentioned the problem, this work investigates adsorption characteristic of hydrogen on kenaf. The objectives of this study are:

- i. To characterize kenaf and modified kenaf as adsorbent.
- ii. To assess adsorptive capacity of adsorbent.
- iii. To assess delivery performance of the adsorptive gas storage.

#### 1.4 Scope of Study

Based on the underlying objectives, kenaf (*Hibiscus cannabinus L.*) was modified using nickel metal ( $\text{Ni(OH)}_3$ ) as modifier. In this study, nickel nitrate ( $\text{Ni(NO}_3)_2$ ) has been used to modify kenaf adsorbent. Then, the study has been continued by selecting the suitable method to modified kenaf adsorbent. The concentration of  $\text{Ni(NO}_3)_2$  added were varied and the characteristics of the adsorbent has been determined. Kenaf has been expected gives higher porosity in its internal structure. This study includes measuring the specific area of raw and modified kenaf by using BET surface area, which could lead the better adsorbent for hydrogen storage. Other than that, characterization of kenaf samples has been conducted for its physical and chemical properties using Thermogravimetric analysis (TGA) to investigate the changes in kenaf before and after modification. Field Scanning Electron Microscopy (FESEM) analysis also has been carried out in this study. It is used to identify the surface structure of raw and modified kenaf. Energy Dispersive X-ray (EDX) analysis also has been implemented in this study in order to observe the behavior change in kenaf chemical content. Eventually, this test would figure out the characteristic of reliable raw kenaf and modified kenaf adsorbent.

This research investigated the potential use of modified kenaf as adsorptive material in hydrogen gas storage. By suitable amount of modifier, the result of the modified adsorbent reacts determined the suitable value for gas storage using kenaf as adsorbent. The adsorptive capability of modified kenaf has been reviewed in order to determine the suitable value of modifier used for kenaf. In order to assess the adsorptive capacity of adsorbent, this study has carried out experiment on adsorbent used to store hydrogen. By measuring the concentration of  $\text{Ni(NO}_3)_2$  added in kenaf modification, it is believed it influenced the amount of hydrogen adsorbed. During the experiment, the storage capacity of kenaf been measured with hydrogen pressure supply from 2 bar to 6 bar. Kenaf adsorbent with different concentrations of  $\text{Ni(NO}_3)_2$ , variation of pressure level (2 bar until 6 bar) and adsorption time (8 hours) were used to determine the performance of hydrogen adsorption.

By carried out the test, performance of overall gas storage has been assessed. In ambient condition, the hydrogen storage was charge and discharged to investigate the delivery performance of storage system. In this study, van der Waals equation has been used in order measuring the hydrogen adsorbed in kenaf adsorbent. This equation has described that pairwise attraction called van der Waals force. The molecules particles were attracted to each other. The attraction force between them has taken into account and described the behavior of real fluids. The van der Waals equation as shown in Equation 1.1.

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (1.1)$$

where,

$P$	–	pressure (Pa)
$V$	–	volume (m <sup>3</sup> )
$T$	–	temperature (K)
$R$	–	gas constant, 8.3144621 J/mol.K
$a, b$	–	specific constant for each gas

For hydrogen gas, a and b specific constant are

$a$	-	0.02476 J.m <sup>3</sup> / mol <sup>2</sup>
$b$	-	2.661 x 10 <sup>-5</sup> m <sup>3</sup> /mol

The best adsorbent that adsorbed high hydrogen gas used for cyclic performance shows modification of kenaf could enhance the capability of kenaf as gas adsorbent by increasing the number of adsorption site on the surface. The amount of hydrogen adsorbed has been calculated by pressure reduced after hydrogen release into the system. Moreover, the effect of parameters is important to be studied such as the modification of kenaf, concentration of modifier, the level of pressure used for hydrogen to be adsorbed and performance of hydrogen adsorption. In this study, performance of hydrogen adsorption was measured in rate of adsorption per gram of kenaf (mmol/g of kenaf).

## 1.5 Significant of Study

Kenaf was introduced as hydrogen adsorbent since it is light with highly porous material. Its role as adsorbent can reduce pressure in hydrogen storage. Kenaf provides large surface area that could adsorb more hydrogen at the average pressure. In addition, dispersion of  $\text{Ni}(\text{NO}_3)_2$  on kenaf surface may enhance the adsorption ability. Nickel metal was known as one of reliable metal adsorbent in industry as good adsorbent for chemical and gas. Therefore, it has been used as modifier in this study and improved the surface characteristic of kenaf. The characteristic of kenaf has also been modified in terms of its physical and chemical structure shown in BET surface area and TGA analysis. Furthermore, the surface and porosity of modified kenaf has been improved and become more structured compared to raw kenaf showed in FESEM analysis. Modified kenaf could adsorb more hydrogen compared using raw kenaf itself because the chances for hydrogen gas to adsorb on modified kenaf higher compared to raw kenaf. The surface area on modified kenaf gave more active site for hydrogen molecules bond within kenaf porous. Hence, findings in this study have given significant improvement in hydrogen adsorption process.

## 1.6 Report Outline

There were five chapters in this report. Introduction of research has been written in first chapter. The background of study, problem statement, objectives of study and scope has been included in this chapter. Significant of study was also included to highlight the benefit of this research. In Chapter 2, literature review written on hydrogen adsorption, the technologies currently used in industries including adsorptive storage, adsorbent used in industries and characteristics on kenaf were presented. Chapter 3 described on materials, methods and procedures used in the experiment. The experimental rig and the fabricated adsorbent reactor and system were also included. In addition, the preparation of kenaf adsorbent and its modification were thoroughly explained. The results were presented and discussed in Chapter 4. In the chapter, discussion on the characteristics of kenaf and modified

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